

A doped diamond-like carbon coating**Field of the invention.**

5 The invention relates to a doped diamond-like carbon coating and to a process for depositing such a coating on a substrate.

Background of the invention.

10 Amorphous hydrogenated carbon (a-C:H), known as diamond-like carbon (DLC), shows several attractive characteristics. Coatings having a diamond-like carbon composition are suitable as hard, wear resistant, self lubricant and corrosion resistant coatings.

15 However, high internal compressive stresses (up to several GPa) are present in the material as a result of which the adherence to the substrate is not always sufficient. This limits the application of this material as coating material.

Because of the high internal stresses, only coatings with a limited thickness may be applied.

20 Another drawback of DLC coatings is that the friction coefficient increases considerably with humidity. This inhibits the application of DLC coatings as low friction coating in humid environment or in water.

Several attempts have been made to improve the adhesion to the substrate.

25 It is known from EP 600 533 that the application of an intermediate silicon layer may improve the adherence of coating with a DLC composition on a steel or iron substrate.

30 WO98/33948 describes the deposition of a diamond-like nanocomposite (DLN) layer on the substrate before the deposition of a DLC layer. DLN coatings comprise generally two interpenetrating networks a-C :H and a-Si:O; and are known as Dylyn®.

Summary of the invention.

35 It is an object to provide a silicon-nitrogen doped diamond-like carbon coating, having a high hardness, a good adhesion to the substrate and which is further characterised by non-sticking properties.

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It is another object to provide a multilayered coating with a good adhesion to the substrate. Moreover, the multilayered coating shows low total internal stresses, even for rather thick coatings.

Further, it is an aim to provide a process for depositing a coating
5 according to the invention on a substrate.

According to a first aspect of the invention a silicon-nitrogen doped diamond-like carbon coating is provided. This coating comprises the elements C, H, Si and N. The concentration ranges of the elements C,
10 Si and N expressed in proportion to the sum of C, Si and N are as follows : 30 to 90 at% C, 5 to 50 at% Si and 5 to 40 at% N. Preferably, the concentration of C is between 40 and 50 at%, the concentration of Si is between 15 and 40 at% and the concentration of N is between 12 and 20 at%.

15 It has been shown that the coating can further contain a small amount of oxygen. This presence can be due to diffusion of oxygen into the coating. The amount is however limited to a few percents maximum and is the highest closest to the outer surface of the coating layer.

20 The adhesion of the coating according to the invention, expressed by means of the critical load, as measured in a scratch test, is greater than 22 N.

The doped diamond-like carbon coating can be considered as a non-sticking coating.
25

A possibility to express the non-sticking behaviour of coatings is by means of their surface energy. In most cases, a low surface energy goes hand in hand with an improvement of the non-sticking characteristics.

30 For the purposes of this application, a coating is considered to have non-sticking characteristics if its surface energy is below 40 mN/m. More

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preferably, the surface energy is below 33 mN/m and most preferably below 30 mN/m.

5 In addition to its non-sticking properties, the coating is characterised by a high hardness. It has been shown that the hardness is higher than 12 GPa. In most cases, the hardness is even higher than 15 GPa.

10 Because of its low surface energy, the coating is very suitable as a coating for a substrate for applications where non-sticking characteristics are desired. Examples are moulds used for plastic injection moulding, tablet or powder punches and implants such as stents.

15 The combination of a low surface energy and a high hardness gives the doped diamond-like carbon coating layer exceptional characteristics and makes this type of coating feasible for many industrial applications.

20 The coating layer can further be doped with one or more additional elements such as fluorine or a transition metal as for example W, Zr or Ti. The presence of metallic doping elements has an influence on the thermal and/or electrical conductivity of the coating. This means that by adding a controlled amount of metallic doping element(s), the thermal and/or electrical conductivity of the coating may be controlled. The presence of doping elements can also be desired to control the surface energy.

25 Also an inert gas, such as Ar, Kr or Ne can be incorporated into the coating composition, by introducing an inert gas in the vacuum chamber during deposition.

30 According to a second aspect, a multilayered coating is provided. This multilayered coating comprises at least one layered structure. Such a layered structure comprises

- a first layer closest to the substrate comprising a silicon-nitrogen doped diamond-like carbon coating comprising the elements C, H, Si and N;
- 5 - a second layer on the top of the first layer comprising a diamond-like carbon composition;
- a transition layer between the first and the second layer comprising a mixture of the silicon-nitrogen doped diamond-like carbon coating and the diamond-like carbon composition.

10 For coatings comprising more than one layered structure, there is an intermediate layer comprising a mixture of the diamond-like carbon composition layer and the doped diamond-like carbon coating, sandwiched between each pair of consecutive layered structures.

15 The transition layer gradually changes from a composition comprising C, H, Si and N to a diamond-like carbon composition layer. The intermediate layer, on the other hand gradually changes from a diamond-like carbon composition layer to a composition comprising C, H, Si and N.

20 From adhesion measurements, it can be concluded that the first layer functions as an excellent adhesion promoting layer for the DLC layer. The critical load is considerably increased in comparison with a DLC composition layer deposited directly on the substrate.

25 Furthermore, the adhesion promoting layer according to the present invention has the advantage over other adhesion promoting layers, such as silicon layers, that it not only offers a good adhesion, but that it is also characterised by a rather high hardness. As a result thereof, the multilayered coating has a hardness which comes close to the hardness of a DLC coating layer.

30 The repeated alternation of a layer comprising C, H, Si and N and a DLC composition layer allows it to deposit thicker coatings, for example coatings with a thickness of more than 10 μm . The number of layered

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structures can vary from 1 to 5000 and is for example situated between 5 and 50.

A multilayered coating according to the present invention shows greatly reduced internal stresses. This is due to the lower Young's modulus
5 (higher elasticity) of the silicon-nitrogen doped diamond-like carbon coating layer sandwiching the DLC coating layer. Even for thick coatings, the total internal stresses of the coating remain low.

10 In order to control the thermal and/or electrical conductivity and/or the surface energy of the coating, any layer of the multilayered coating can be doped, for example with fluorine or with a transition metal.

Depending on the desired properties of the multilayered coating and depending on the application, the outer top layer of the coating may be
15 varied.

When a DLC layer is deposited on top of the multilayered coating, the hardness and low-wear characteristics, typical for a DLC type coating prevail. This implies that by depositing a DLC layer on top of a
20 multilayered coating a high wear and abrasion resistance coating is obtained. Thicknesses higher than these of conventional DLC coatings can be deposited in this way. Possible fields of applications are the coating of metal forming tools and textile needles.

In the case a doped diamond-like carbon coating comprising the elements C, H, Si and N is deposited on the top, the multilayered coating is
25 characterised by a low surface energy and by a low friction coefficient. The non-sticking properties of such a coating, make it suitable for many applications, in particular as a coating for plastic injections moulds and powder pressing tools.

30 Other possibilities for the outer layer are for example a layer comprising C, H, Si and O; a Si-C doped layer; a C-F doped layer; a Si-F-C doped layer or a Si-F-O-C doped layer.

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According to a third aspect a substrate coated with a doped diamond-like carbon coating or with a multilayered coating according to the invention is provided.

5 This substrate could be rigid or flexible. Possible substrates are hardened steel (e.g. 100Cr-6), aluminium, silicon, titanium or glass.

According to a further aspect a process for coating a substrate at least in part is provided.

10 The substrate is brought into the vacuum chamber and is fixed to the substrate plate by any suitable means.

Preferably, the surface of the substrate is cleaned before the deposition of the coating. This can, for example, be done by bombarding the substrate with ions of an inert gas such as Ar, Kr or Ne. This
15 pretreatment activates the surface and removes residual impurities from the substrate surface.

A precursor or a mixture of different precursors, comprising the elements C, H, Si and N, is brought into the vacuum chamber, a plasma is formed
20 from the introduced precursor and the composition of the plasma is deposited on the substrate to which a negative bias voltage has been applied.

25 Once the substrate has been coated with an adhesion layer of sufficient thickness, the process further comprises the following steps.

The precursor composition is gradually exchanged by a hydrocarbon without stopping the glow discharge. Subsequently, the plasma is formed from the mixture of the precursor and the hydrocarbon and a transition layer from said mixture is deposited on the substrate to which a
30 negative bias voltage has been applied. The mixture gradually changes from a composition comprising the elements C, H, Si and N to a

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diamond-like carbon composition, comprising only the elements C and H.

Once the coating comprises a diamond-like carbon composition, the plasma deposition is continued to deposit a diamond-like carbon composition layer from the hydrocarbon until the desired thickness is obtained.

When the multilayered coating comprises more than one layered structure, the process further comprises, for each additional layered structure, the steps of

- gradually exchanging said hydrocarbon by a precursor comprising the elements C, H, Si and N, forming continuously a plasma from the hydrocarbon and said precursor and depositing an intermediate layer from said mixture;
- continuing the plasma deposition from the precursor comprising the elements C, H, Si and N;
- gradually exchanging said precursor by a hydrocarbon;
- depositing a DLC composition layer from said hydrocarbon.

The plasma may be generated and deposited on the substrate in different ways.

A first possible method to generate a plasma is by means of a capacitively coupled radiofrequency glow discharge (RF) applied to the substrate. The frequency is chosen between 1 MHz and 28 MHz, and is preferably 13.56 MHz. A bias voltage between 50 and 1000 V is applied to the substrate.

Another possible method to generate the plasma is by applying a negative DC-bias or midfrequency (MF) bias voltage of 200 to 1200 V to the substrate. The frequency of the MF bias voltage can vary between 30 and 1000 kHz.

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More preferably, the plasma is generated by an electron assisted discharge. The filament current is preferably between 50 and 150 A, the negative filament bias DC voltage between 50 and 300 V and the plasma current between 0.1 and 20 A.

5

A further possibility to generate the plasma is by means of a bipolarly pulsed DC source.

"Bipolarly" means that a negative and a positive voltage pulse are applied alternately.

10

Either symmetrical bipolar pulses (equal amplitude for positive and negative pulse) or asymmetric bipolar pulses (amplitude of the voltage during negative pulse higher than the amplitude of the voltage during positive pulse) can be used.

15

By applying a magnetic field during the deposition of the coating, the plasma is further intensified. The magnetic field can be applied by means of an inductive coil. The magnetic field is preferably between 10 and 30 Gauss.

20

It has been shown that a silicon-nitrogen doped diamond-like carbon coating deposited by using a RF with a high frequency, for example 13.56 MHz shows very good non-sticking characteristics.

25

A liquid or gaseous component comprising the elements C, H, Si and N to be deposited in suitable proportions can be used as precursor.

A preferred precursor is a silazane such as 1,1,3,3-tetramethyldisilazane or hexamethyldisilazane.

30

In an alternative way the precursor can be a mixture of different components, for example a mixture of a silane, a hydrocarbon and nitrogen gas in such a way that the mixture comprises the elements C, H, Si and N in suitable proportions.

The hydrocarbon can be a saturated or an unsaturated acyclic or cyclic hydrocarbon, with the number of carbon atoms varying from 1 to 20. Also substituted hydrocarbons are suitable as precursor.

5 Examples of precursors are methane, propane, butane, pentane, cyclopentane, ethylene, acetylene and aromatic or substituted aromatic hydrocarbons such as benzene and substituted benzene.

The pressure in the vacuum chamber is between $1 \cdot 10^{-3}$ and 1 mbar and preferably between $5 \cdot 10^{-3}$ and $1 \cdot 10^{-1}$ mbar, for example $2 \cdot 10^{-2}$ mbar.

10 The flow of the precursor may vary between 0.1 g/hour and 25 g/hour. Preferably, the flow of the precursor is between 1 and 3 g/hour. The flow of the inert gas, for example Ar, is between 10 and 500 ml/min. Preferably, the precursor and the argon gas are introduced into the vacuum chamber in a controlled way by means of a controlled
15 evaporation and mixing system (CEM). The CEM system allows it to control the precursor flow as well as the argon flow independently of each other. By the CEM system, the process can be controlled easily. The deposition time may be varied according to required thickness.

20 **Brief description of the drawings.**

The invention will now be described into more detail with reference to the accompanying drawings wherein

- FIGURE 1 shows a substrate coated with a silicon-nitrogen doped diamond-like carbon layer.
- 25 - FIGURE 2, 3 and 4 show substrates coated with different types of multilayered coatings.

Description of the preferred embodiments of the invention.

30 With reference to the drawings, some preferred coating types are described.

With regard to figure 1, a substrate 11 is coated with a silicon-nitrogen doped diamond-like carbon coating 12 by means of a RF glow discharge. The substrate was brought in the vacuum chamber and was fixed to the substrate plate.

The surface of the substrate was cleaned by plasma etching the substrate by means of Ar ions during 10 minutes. After the cleaning 1,1,3,3-tetramethyldisilazane was introduced into the vacuum chamber at a flow rate of 1.8 g/hour, whereas Ar was introduced at a flow rate of 75 ml/min. The disilazane precursor and the argon gas were introduced into the vacuum chamber in a controlled way by means of a controlled evaporation and mixing system (CEM).

In order to generate the plasma, a radiofrequency of 13.56 MHz was applied to the substrate plate. The bias voltage was 300 V.

The pressure in the vacuum chamber was $1.6 \cdot 10^{-2}$ mbar. The deposition was carried out during 60 minutes.

The composition of the coating layer deposited on the substrate is determined by X-ray Photoelectron Spectroscopy (XPS). The coating has a carbon content of 43 at%, a silicon content of 40 at% and a nitrogen content of 14 at%. The concentration of hydrogen is left out of consideration. It has been shown that a small amount of oxygen, namely 3%, is present.

The non-sticking properties are evaluated by determining the surface energy of the coating and the contact angle of a water droplet on a coated surface.

The measurement of the contact angle of a water droplet on the coated substrate gives a contact angle of 81° .

The surface energy of the deposited coating equals 30.5 mN/m. The dispersive component is 24.9 mN/m, the polar component is 5.8 mN/m.

The hardness is determined by a nano-indentation test. The penetration depth was 300 nm. By this method the nanohardness is determined to be 15.8 ± 0.4 GPa.

The adhesion of the coating is determined by carrying out a scratch test.

5 The scratch experiments are performed on 4 cm² M2 steel plates. The critical load (L_{c2}), where the first hints of delamination can be seen, was 22 N.

Furthermore, the coating is characterised by a high elasticity, which is expressed by Young's modulus. This modulus is determined to be $125 \pm$
10 2 GPa.

In an alternative method a coating layer comprising the elements C, H, Si and N as shown in figure 1, is deposited on a substrate by means of an electron assisted DC-discharge in combination with a MF bias applied
15 to the substrate.

Argon was introduced in the vacuum chamber in order to clean and activate the substrate surface.

Subsequently, 1,1,3,3-tetramethyldisilazane was introduced into the vacuum chamber at a flow rate of 7.2 g/hour, while Ar was introduced at
20 a flow rate of 500 ml/min. The flow rates are controlled by a CEM system.

The plasma is generated from a heated filament in combination with a DC bias applied on the substrate.

The bias voltage on the substrate was 600 V. The plasma current was 1
25 A, the negative filament bias DC voltage was 100 V.

The plasma was intensified by applying a magnetic field. The magnet current was 5 A.

The pressure in the vacuum chamber was $8.5 \cdot 10^{-3}$ mbar. The coating layer was deposited during 60 minutes.
30

The composition of the deposited layer was determined by XPS. The composition of the coating is as follows : 45.2 at% C, 15.2 at% N and

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39.7 at% Si. These concentrations are expressed in proportion to the sum of C, N and Si.

Similar experiments were performed using the following parameters :

5	Tetramethyldisilazane flow :	10.3 g/hour
	Argon flow :	500 ml/min
	Bias voltage :	200 V
	Filament bias :	100 V
	Magnet current :	5 A
10	Pressure :	$8.5 \cdot 10^{-3}$ mbar
	Deposition time :	60 min

After analysis by XPS, it has been shown that the coating comprises 46.0 at% C, 16.1 at% N and 37.9 at% Si, expressed in proportion to the sum of C, N and Si.

15

Figure 2 represents a substrate 11 coated with a multilayered coating 13. This coating comprises a first layer 14 closest to the substrate comprising C, H, Si and N, and a second DLC composition layer 15. Between the first and the second layer, there is a transition layer 16, gradually changing from a layer comprising the elements C, H, Si and N to a layer with a DLC composition.

20

For the deposition of the first layer of the bilayered coating, tetramethyldisilazane was introduced in the vacuum chamber at a flow rate of 1.8 g/hour, argon was introduced at a flow rate of 75 ml/hour. A RF of 13.56 MHz was applied to the substrate, the bias voltage was 300 V. In the vacuum chamber there was a pressure of $1.6 \cdot 10^{-2}$ mbar. The first layer was deposited during 30 minutes.

25

After the deposition of the first layer, the 1,1,3,3-tetramethyldisilazane precursor was gradually exchanged by CH_4 .

30

In order to deposit a DLC composition layer, CH_4 was introduced in the vacuum chamber at a flow rate of 80 ml/min, together with H_2 at a flow rate of 20 ml/min.

The bias voltage was 350 V, the pressure in the vacuum chamber $1 \cdot 10^{-2}$ mbar. The deposition time of the DLC composition layer was 120 minutes.

The total thickness of the multilayered coating is 2.5 μm .

5

The deposited bilayered coating has a hardness of 21.4 ± 0.7 GPa.

A scratch test, measured on a 4 cm^2 M2 steel plate, showed a critical load, L_{c2} of 25.7 ± 4 N.

Young's modulus is determined to be 135 ± 2 GPa .

10

It can be concluded from the adhesion measurement that the first layer offers the coating an excellent adhesion to the substrate. The critical load is considerably increased in comparison with a DLC layer deposited directly on the substrate.

15

Furthermore, the bilayered coating is characterised by a high hardness.

An alternative method for depositing a bilayered coating as represented in figure 2 is as follows.

20

A tetramethyldisilazane precursor is introduced in the vacuum chamber at a flow rate of 7.2 g/hour. Argon is added as a carrier gas at a flow rate of 500 ml/min. A bias voltage of 500 V is applied to the substrate. The plasma current was 1 A, the filament bias 100 V and the magnet current 5 A. The pressure in the vacuum chamber was $8.5 \cdot 10^{-3}$ mbar. The first layer is deposited during 30 minutes.

25

Subsequently, the tetramethyldisilazane precursor is exchanged by C_4H_{10} precursor. A bias voltage of 600 V is applied to deposit the DLC composition layer. This DLC composition layer was deposited during 3 hours. The thickness of the coating was 1.3 μm .

30

The bilayered coating obtained in this way demonstrates a high hardness (21 GPa). Adhesion measurements by performing a scratch test on a 4 cm^2 M2 steel plate showed a critical load of 28 ± 0.7 N.

Figure 3 shows a substrate 11 coated with a multilayered coating 13. This coating comprises a first layer 14 comprising C, H, Si and N, a second layer 15 comprising a diamond-like carbon composition deposited on the first layer and a third layer 18 with the same composition as the first layer deposited on the top of said second layer. A transition layer 16 is situated in between the first and the second layer. Between the second and the third layer, there is an intermediate layer. The first layer, closest to the substrate, functions as an adhesion promoting layer. The DLC composition layer deposited on this adhesion promoting layer gives the multilayered coating the required hardness. Finally, the outer layer deposited on the DLC composition layer gives the coating the desired non-sticking properties. Total internal stresses of the coating are low.

Figure 4 shows a multilayered coating 13 comprising two layered structures 19. Each layered structure comprises closest to the substrate a first coating layer 14 comprising the elements C, H, Si and N, a second DLC composition layer 15 deposited on top of the first layer and a transition layer between said first and second layer. In between the two consecutive layered structures, there is an intermediate bonding layer 17.

If the multilayered coating comprises more layers, the above described steps could be repeated.

CLAIMS

1. A silicon-nitrogen doped diamond-like carbon coating (12), said
coating comprising 30 to 90 at% C, 5 to 50 at% Si and 5 to 40 at% N,
5 these concentrations being expressed in proportion to the sum of all
elements being part of the coating with the exception of H, said
coating having an adhesion, expressed by means of the critical load,
as measured in a scratch test, greater than 22 N.
- 10 2. A coating according to claim 1, comprising in proportion to the sum of
all elements being part of the coating with the exception of H, 40 to
50 at% C, 15 to 40 at% Si and 5 to 40 at% N.
- 15 3. A coating according to claim 1 or 2, whereby the hardness is greater
than 15 GPa.
4. A coating according to any one of claims 1 to 3, whereby the surface
energy is less than 40 mN/m.
- 20 5. A coating according to any one of claims 1 to 3, whereby the surface
energy is less than 33 mN/m.
- 25 6. A coating according to claim 1 or 2, whereby the surface energy is
less than 33 mN/m and whereby the hardness is greater than 15
GPa.
- 30 7. A coating according to any one of claims 1 to 6, whereby said
coating is doped with fluorine and/or with at least one transition
metal.
8. A multilayered coating (13) comprising at least one layered structure
(19), each layered structure comprising

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- a first layer (14) closest to the substrate comprising a silicon-nitrogen doped diamond-like carbon coating according to any one of claims 1 to 7;
 - a second layer (15) on the top of said first layer comprising a diamond-like carbon composition;
 - a transition layer (16) between said first and said second layer comprising a mixture of said doped diamond-like carbon coating and said diamond-like carbon composition.
9. A multilayered coating according to claim 8, comprising at least two layered structures, whereby an intermediate layer (17) comprising a mixture of said doped diamond-like carbon coating and said diamond-like carbon composition being sandwiched between each pair of consecutive layered structures.
10. A multilayered coating according to claims 8 or 9, whereby a silicon-nitrogen doped diamond-like carbon coating (18) according to any one of claims 1 to 8 is present on the top of said coating.
11. A multilayered coating according to claims 8 or 9, whereby at least one of said layers is doped with fluorine and/or with a transition metal.
12. A multilayered coating according to any one of claims 8 to 11, whereby the total thickness of the coating is between 2 and 20 μm .
13. A substrate covered at least partially with a coating according to any one of claims 1 to 12.
14. A process for coating in a vacuum chamber a substrate at least in part, said process comprising the steps of

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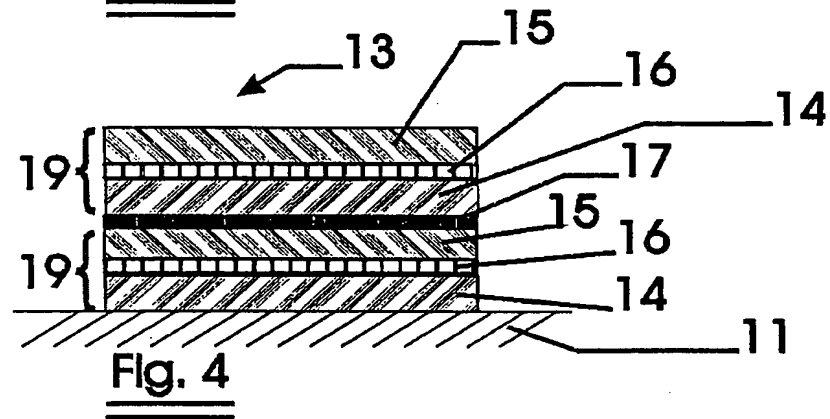
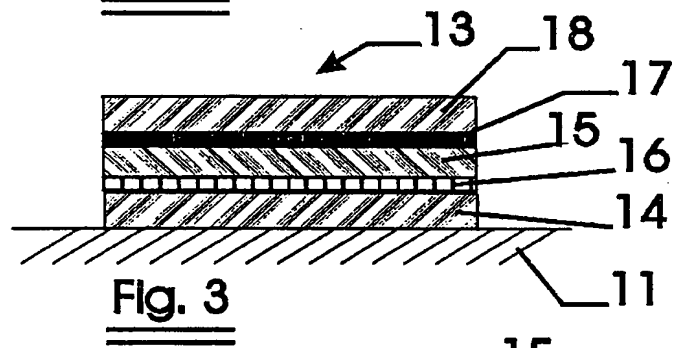
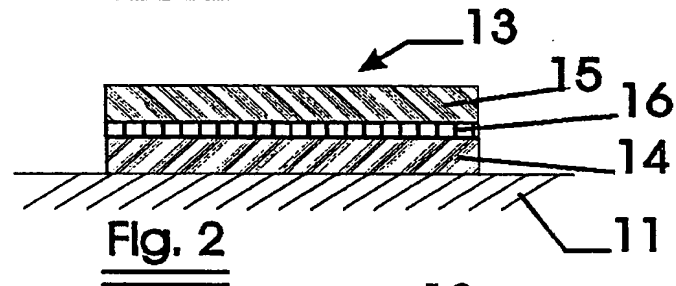
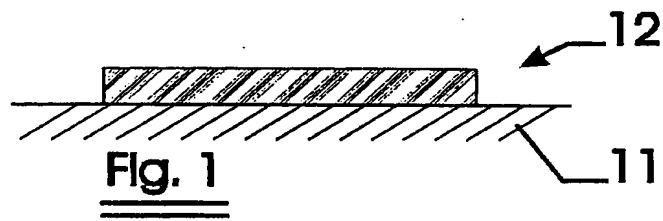
- a. plasma etching the substrate by bombardment of the substrate by ions of an inert gas;
 - b. introducing in the vacuum chamber a precursor comprising the elements C, H, Si and N to be deposited in suitable proportions,
5 forming a plasma from the introduced precursor and depositing the composition of the plasma on the substrate to which a negative bias voltage is applied.
15. A process for coating a substrate according to claim 14 further comprising the steps of
- c. gradually exchanging said precursor by a hydrocarbon, forming a plasma from the mixture of the precursor and the hydrocarbon, and depositing a transition layer from said mixture on the substrate to which a negative bias voltage is applied;
 - 15 d. continuing the plasma deposition of the diamond-like carbon composition layer from said hydrocarbon.
16. A process according to claim 15, further comprising for each additional layered structure (19) of the coating, the steps of
- 20 e. gradually exchanging said hydrocarbon by a precursor comprising the elements C, H, Si and N, forming a plasma from the hydrocarbon and said precursor and depositing an intermediate layer from said mixture;
 - f. continuing the plasma deposition from the precursor comprising the
25 elements C, H, Si and N;
 - g. gradually exchanging said precursor by a hydrocarbon;
 - h. depositing a diamond-like carbon composition layer from said hydrocarbon.
17. A process according to any one of claims 14 to 16, whereby a
30 radiofrequency between 1 and 28 MHz is applied on the substrate.

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18. A process according to any one of claims 14 to 16, whereby a negative DC bias or a MF bias voltage of 200 to 1200 V is applied to the substrate.
- 5 19. A process according to any one of claims 14 to 16, whereby a pulsed DC bias voltage is applied to the substrate.
20. A process according to claim 18, whereby the frequency of the MF bias voltage is between 30 and 1000 Hz.
- 10 21. A process according to any one of claims 18 to 20, whereby said plasma is a stimulated plasma using electron emission from a filament.
- 15 22. A process according to claim 21, whereby said electron emission is obtained by an electron assisted discharge using a filament current of 50 to 150 A, a negative filament DC bias voltage of 50 to 300 V and a plasma current between 0.1 and 20 A.
- 20 23. A process according to any one of claims 18 to 22, whereby a magnetic field is applied to intensify the plasma.
24. A process according to any one of claims 14 to 23, whereby said precursor containing C, H, Si and N is a silazane.
- 25 25. A process according to claim 24, whereby said silazane is 1,1,3,3-tetramethyldisilazane or hexamethyldisilazane.
- 30 26. A process according to claim 25, whereby the hydrocarbon is selected from the group comprising saturated and unsaturated acyclic or cyclic hydrocarbons comprising 1 to 20 C atoms.

27. A process according to claim 26, whereby the cyclic hydrocarbon is benzene or a substituted benzene.

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INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/EP 00/04438

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/30 C23C28/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, INSPEC, IBM-TDB, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 249 554 A (TAMOR MICHAEL A ET AL) 5 October 1993 (1993-10-05)	14, 15, 18
Y	column 8, line 29 - column 11, line 14 ---	19, 24-27
X	DE 37 02 242 A (HOCHVAKUUM DRESDEN VEB) 17 September 1987 (1987-09-17) column 2, line 30 - line 50 column 3, line 20 - line 56 ---	14
Y	FRACASSI F ET AL: "PECVD OF SIOXNYCZHW THIN FILMS FROM HEXAMETHYLDISILAZANE CONTAINING FEED. INVESTIGATION ON CHEMICAL CHARACTERISTICS AND AGING BEHAVIOR" PLASMAS AND POLYMERS, US, PLENUM PRESS, vol. 2, no. 1, page 25-40 XP000753293 ISSN: 1084-0184 paragraph '0002! --- -/-	24-27



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/EP 00/04438

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 712 000 A (MATOSSIAN JESSE N ET AL) 27 January 1998 (1998-01-27) column 5, line 35 - line 45 ----	19
A	WO 95 24275 A (DIAMONEX INC) 14 September 1995 (1995-09-14) page 10, line 3 - line 17 page 12, line 21 - line 30 page 16, line 3 -page 17, line 10 ----	1-27
A	DE 44 20 262 A (ZEXEL CORP) 15 December 1994 (1994-12-15) claims 1-13 ----	1-27
A	WO 98 33948 A (BEKAERT SA NV ;PERSOONE PETER (BE); NEERINCK DOMINIQUE (BE)) 6 August 1998 (1998-08-06) cited in the application claims 1-22 ----	1-27
A	EP 0 625 588 A (FRAUNHOFER GES FORSCHUNG) 23 November 1994 (1994-11-23) example 1; table 1 -----	5-8

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Information on patent family members

International Application No

PCT/EP 00/04438

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